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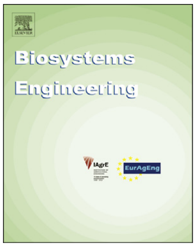

Research Paper

Thermal behaviour and kinetic study for woody biomass torrefaction and torrefied biomass pyrolysis by TGA

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The thermal decomposition behaviour and kinetics of Douglas fir sawdust torrefaction and torrefied sawdust pyrolysis were investigated using a thermogravimetric analyser (TGA). The mass loss of samples in torrefaction was highly related to the torrefaction temperature. The two-step reaction model fitted well for Douglas fir sawdust torrefaction. The activation energies of the first and second reaction stages were 112 kJ mol^{-1} and 150 kJ mol^{-1}, respectively. Torrefied biomass exhibited different thermo decomposition behaviours compared to untreated biomass. The start point of torrefied biomass decomposition was shifted and the degree of shift increased with the severity of torrefaction. The final biochar yield of torrefied biomass was also increased with the increase of torrefaction temperature. Derivative thermogravimetric (DTG) curves showed that the shoulder of hemicelluloses decomposition in torrefied biomass pyrolysis was eliminated. The decomposition rate of torrefied biomass has a decreasing trend due to the mass depletion in torrefaction. A first-order one-step global model with the average activation energies in the range of 195–204 kJ mol^{-1} can describe the raw and torrefied biomass pyrolysis. The kinetic analysis also showed that the torrefied biomass pyrolysis from high torrefaction temperature might be multiple-step reactions.

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1. Introduction

Fossil fuels have in the past played an important role in transportation fuel supplies and continue to do so. However, fossil fuels are not renewable and the declining limited reserves and the increasing demand for fossil fuels has led to the global energy crisis. The contribution of the greenhouse gases emission by burning fossil fuels has also brought a major environmental challenge. These problems motive scientists to search for alternative energy. Biomass is an abundant and carbon-based renewable fuel resource that can provide a continuous energy supply by annually planting and harvesting. Biomass is also a clean and carbon-neutral energy source as its carbon is recycled from the atmosphere (Ragauskas et al., 2006).

Biomass has high water and oxygen content as well as low bulk density and heating value. These properties hinder its broad utilisation. Several technologies have been used to convert biomass to high-energy fuels in the form of solids, liquids, and gases. These technologies include torrefaction,

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Nomenclature

k	rate coefficient, min^{-1}
n	order of reaction
α	mass change of sample, mg
X_0	initial sample weight, mg
X	sample weight at time t, mg
X_f	final sample weight, mg
A	frequency or pre-exponential factor, min^{-1}
E	apparent activation energy, J mol^{-1}
T	temperature, K
R	universal gas constant, 8.3145 J mol^{-1} K^{-1}
t	time, min
s	sum of squared deviations
N	total number of points
i	an index, from 1 to N
$(X_t)_{exp,i}$	observed mass value, mg
$(X_t)_{calc,i}$	calculated mass value, mg

pyrolysis, liquefaction, digestion, fermentation, and gasification, among which torrefaction and pyrolysis are thermo-chemical methods. Torrefaction, also called mild pyrolysis, is conducted at the temperature of 200–300 °C in an inert environment to convert biomass to solid fuels (Bergman & Kiel, 2005). In comparison, biomass pyrolysis is a strong thermo-chemical method conducted at the temperature of 350–600 °C in inert environment (Scott & Piskorz, 1984). The primary product of biomass pyrolysis is bio-oil. During the thermo-chemical processes, thermal decompositions of biomass are involved.

Biomass is complex, composed primarily of hemicelluloses, cellulose, and lignin. In pyrolysis, these three components of biomass are decomposed at different temperatures and rates. The hemicelluloses and cellulose can be decomposed relatively fast at low temperatures of 200–350 °C while lignin are decomposed slowly in a wide range of temperatures from 280 to 600 °C (Mohan, Pittman, & Steele, 2006). As a result, the thermal decomposition and reaction kinetics of biomass are complicated. The developed models in biomass pyrolysis are generally categorised as one-step global or semi-global models and multiple-step reaction models (Blasi, 2008; White, Catallo, & Legendre, 2011). Shafizadeh and Chin (1977) proposed the one-step reaction mechanism for biomass pyrolysis by postulating one component of biomass. Blasi (1998) proposed semi-global reaction models for woody biomass pyrolysis in which three parallel reactions for the main components of the biomass would take place in pyrolysis. Bradbury Sakai, and Shafizadeh (1979) proposed the multi-step reactions for cellulose pyrolysis in which cellulose is assumed to be first converted to active cellulose and then decomposed to volatiles and char. The char would be further degraded. Alves and Figueiredo (1989) proposed another mechanism, which consisted of three first-order consecutive reactions.

Torrefaction as a mild pyrolysis technology at relatively low reaction temperatures of 200–300 °C shows different decomposition mechanisms from biomass pyrolysis. Biomass torrefaction mainly decomposes hemicelluloses and partially degrades cellulose and lignin. Prins, Ptasinski, and Janssen (2006) studied the weight loss kinetics of willow biomass torrefaction with their results confirming to the two-stage mechanism proposed by Blasi and Lanzetta (1997). They showed that the first step of torrefaction was fast with the hemicellulose decomposition and the second step was relatively slow with cellulose decomposition. Chen and Kuo (2011a) investigated the isothermal torrefaction kinetics of the basic constituents of biomass and demonstrated their developed model could properly describe their experiment.

Recently biomass torrefaction as a pretreatment in pyrolysis has drawn increasing attention. The torrefied biomass pyrolysis exhibits different decomposition behaviours due to the removal of hemicelluloses and modification of cellulose and lignin in torrefaction (Chen & Kuo, 2010; Wannapeera, Fungtammasan, & Worasuwannarak, 2011). The cross-linking reaction also occurs in torrefied biomass thermal decomposition leading to more biochar produced (Broström, Nordin, Pommer, Branca, & Blasi, 2012; Ren et al., 2013; Wannapeera et al., 2011). However, studies on the kinetics of torrefied biomass pyrolysis have been lacking. Therefore, the aim of this study was to investigate woody biomass torrefaction and torrefied woody biomass decomposition behaviour and to develop kinetic models from thermogravimetric analysis.

2. Materials and methods

2.1. *Materials*

Douglas fir sawdust pellets purchased from Bear Mountain Forest Products Inc., Brownsville, OR, USA were used as raw materials for torrefaction. The pellets were made from 100% natural Douglas fir wood sawdust and their properties can be found in our previous reports (Ren et al., 2012, 2013). The moisture content of raw Douglas fir pellet was 4.82%.

Three samples of torrefied Douglas fir sawdust pellets were prepared using a bench-scale microwave reactor with different reaction temperatures of 250, 275, and 300 °C, but the same reaction time of 10 min at the power input of 600 W. The proximate analysis and high heating values of torrefied biomass were shown in Table 1. All samples were ground to 2 mm before the thermogravimetric analysis.

2.2. *Thermogravimetric analysis of Douglas fir sawdust torrefaction*

The thermal degradation behaviour of Douglas fir sawdust torrefaction was analysed by TGA (Mettler Toledo 188

Table 1 – Properties of torrefied Douglas fir pellets from different torrefaction temperatures.

Characteristics		Torrefied biomass		
		250 °C	275 °C	300 °C
Proximate analysis (mass%)	Moisture	2.57	2.35	2.00
	Volatile matter	67.88	63.02	50.01
	Fixed carbon	29.34	34.42	47.78
HHV (MJ kg^{-1})		20.90	21.59	23.25

TGA/SDTA 851, Switzerland). The TG analysis was performed at the nitrogen atmosphere with a flow rate of 20 ml/min. For each test, about 10 mg sample was loaded into the crucible. The heating rate was 40 °C/min which was similar to that used in the microwave torrefaction for torrefied biomass preparation (Ren et al., 2012). The torrefaction of samples was performed at temperatures of 250, 275, and 300 °C. After the desired temperature was reached, the samples were held for 1 h.

2.3. Thermogravimetric analysis of torrefied Douglas fir sawdust pyrolysis

The same thermogravimetric analyser was used to perform the thermogravimetric analysis for torrefied biomass pyrolysis. The selected heating rates were 10, 20, 30, 40, and 50 °C/min. The analysis for torrefied biomass was programmed from 25 to 600 °C with a nitrogen flow rate of 20 ml/min. For each test, 10 mg samples were used.

2.4. Biomass decomposition kinetics

In general the reaction rate ($d\alpha/dt$) in kinetics analysis is a function of the remaining raw material (Varhegyi & Antal, 1989)

$$\frac{d\alpha}{dt} = k(1-\alpha)^n \tag{1}$$

where k is reaction coefficient, n is the order of reaction, and the fractional reaction α is defined in terms of the change in mass of samples:

$$\alpha = \frac{X_0 - X}{X_0 - X_f} \tag{2}$$

where X_0 is the initial sample weight, X is the sample weight at time t, and X_f is the final sample weight.

The rate of decomposition follows the Arrhenius law dependent on temperature:

$$k = A\exp(-E/RT) \tag{3}$$

and, Eq. (1) can be expressed as:

$$\frac{d\alpha}{dt} = A\exp(-E/RT)(1-\alpha)^n \tag{4}$$

where A is frequency or pre-exponential factor of the torrefaction process (min^{-1}), E is apparent activation energy (J mol^{-1}), T is temperature (K), R is universal gas constant, 8.3145 ($\text{J mol}^{-1}\ \text{K}^{-1}$), n is the order of reaction, and t is time (min).

3. Results and discussion

3.1. Thermal decomposition behaviour of Douglas fir sawdust torrefaction

Figure 1 shows the thermogravimetric (TG) curves for different torrefaction processes. The curves in Fig. 1 can be divided into two stages (Prins et al., 2006). At first a rapid loss of mass occurred during the heating period and also during the first few minutes of the isothermal process. After that, the mass loss slowed and was linearly proportional at the isothermal torrefaction with slow weight loss. The sample mass loss in torrefaction was significantly influenced by the reaction temperature. At 250 °C, of the mass loss was about 12%, indicating mild decomposition. At 275 °C, the mass loss was about 26%, much greater than at 250 °C. At 300 °C, the sample weight loss was up to 48%, suggesting the decomposition of cellulose and lignin in biomass in addition to the hemicelluloses. These results were consistent with the findings of Prins et al. (2006) and Chen and Kuo (2010, 2011b).

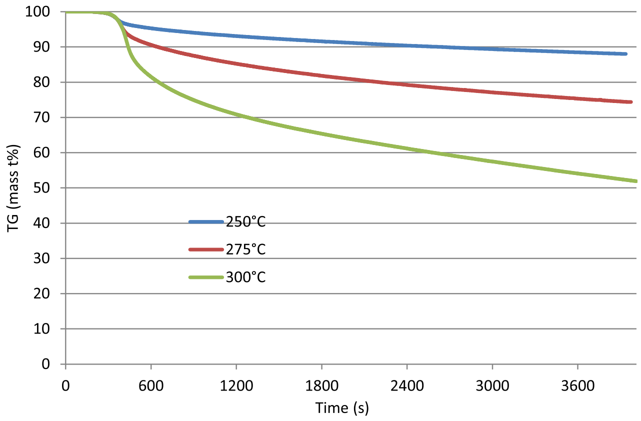

Fig. 1 – TG curves of Douglas fir sawdust torrefaction at different temperatures.

The peaks of the derivative thermogravimetric (DTG) were close to the temperature of the setting point of torrefaction (Fig. 2) and the height of peaks significantly increased with the increase of the torrefaction temperature. Chen and Kuo (2011b) studied the hemicelluloses, cellulose, and lignin decomposition behaviour by TGA and reported that most of hemicelluloses decompose between 250 and 275 °C, and rapid reductions in cellulose occurred from torrefaction at 300 °C. In our research, we observed a rather low mass loss and the peak of the DTG curve occurred at a torrefaction temperature of 250 °C, most likely a result of the predominant decomposition of hemicelluloses. At 275 °C, the mass loss and the height of the DTG peak were doubled compared to those at 250 °C,

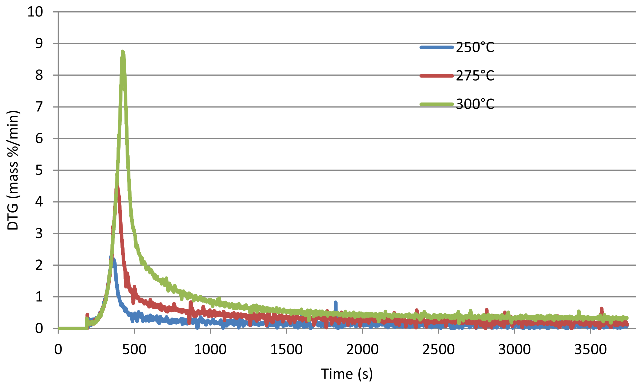

Fig. 2 – DTG curves of Douglas fir sawdust torrefaction at different temperatures.

suggesting the decomposition of both hemicellulose and cellulose of the biomass. At 300 °C, a high mass loss and high DTG peak were observed, indicating that the three components of biomass, especially hemicellulose and cellulose, were all largely decomposed.

3.2. *Isothermal kinetics of Douglas fir sawdust torrefaction*

In the thermogravimetric analysis of torrefaction, the temperature programme consisted of two temperature heating periods. One was the dynamic heating period in which the sample was heated from 25 °C to the desired temperature. Another was the isothermal heating period in which the sample was held at the desired temperature to complete the torrefaction. In this study, the heating rate of 40 °C/min was used to minimise the dynamic heating period to about 6 min. Considering the long isothermal heating period (60 min) compared to the short dynamic heating period (about 6 min), the torrefaction process may be considered an isothermal reaction.

Blasi and Lanzetta (1997) proposed a two-step reaction mechanism for xylan torrefaction using isothermal TGA. In their model volatiles and intermediate components are formed in the first-step reaction, and the intermediate components are decomposed to volatiles and biochar in the second-step reaction. Based on this model, Prins et al. (2006) investigated the weight loss kinetics of willow wood torrefaction in isothermal conditions and determined the parameters of kinetics.

As described previously, Douglas fir sawdust exhibited a two-step mass loss. Hence, the two-step reaction model developed by Blasi and Lanzetta (1997) was used to describe Douglas fir sawdust torrefaction in this study (Fig. 3). Both reactions were assumed to be first-order. The parameters were estimated by the least-squares method by minimising the sum S:

$$S = \sum_{i}^{N} \left((X_t)_{\mathrm{exp},i} - (X_t)_{\mathrm{calc},i} \right)^2 \tag{5}$$

where i is an index, from 1 to the total number of points N, $(X_t)_{\mathrm{exp},i}$ is the ith observed mass value and $(X_t)_{\mathrm{calc},i}$ the calculated mass value obtained by numerical solution with the given parameters. The parameters of initial set were based on Prins et al. (2006)'s findings.

The percent average deviation was calculated as

$$\text{Deviation }(\%) = 100 \cdot \sqrt{S/i} \tag{6}$$

The percent average deviation was 2.41, implying that the model fitted the data well. The activation energy for the first stage of reaction was 112 kJ mol^{-1} (Table 2), which was slightly higher than the values found in Blasi and Lanzetta (1997) and Prins et al. (2006) for willow and xylan torrefaction. The differences might be due to the different properties of samples. The activation energy for the second stage of reaction was 150 kJ mol^{-1} (Table 2), very close to the values obtained in the aforementioned studies, possibly because the decomposition of intermediate components to biochar in different samples tends to be similar.

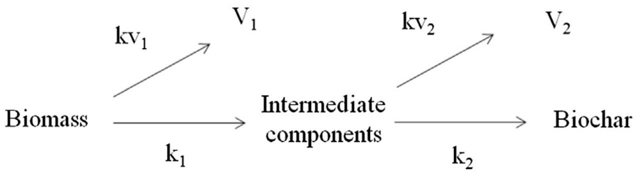

Fig. 3 – Two-step reaction model of biomass torrefaction.

Table 2 – Kinetic parameters determined from the least-square evaluation.

Parameters	Douglas fir sawdust
A_1 (min^{-1})	3.02×10^2
A_{1v} (min^{-1})	5.38×10^5
A_2 (min^{-1})	1.8×10^8
A_{2v} (min^{-1})	2.66×10^8
E_1 (kJ mol^{-1})	113
E_{1v}(kJ mol^{-1})	111
E_2 (kJ mol^{-1})	151
E_{2v} (kJ mol^{-1})	148

3.3. *Thermal decomposition behaviour of torrefied Douglas fir sawdust*

As the TG curves (Fig. 4) revealed, the decompositions of torrefied biomass shifted to a higher temperature and the degree of the shift increased with the severity of torrefaction. For raw biomass, 5% mass loss was observed at the temperature of 278 °C, but for the torrefied biomass the same loss was obtained at 300 °C, and the temperature of decomposition was increased to 313 °C. This phenomenon might be due to the hemicelluloses removal in torrefaction process. The final solid (biochar yield) of raw and torrefied biomass pyrolysis also showed significant differences (Fig. 4). The biochar yield increased substantially with the torrefaction temperature. The raw biomass pyrolysis yielded 21% of biochar, and the torrefied biomass pyrolysis yielded 30%, 35%, and 49% of biochar at torrefaction temperatures of 250, 275, and 300 °C, respectively. The high biochar yield obtained for the torrefied

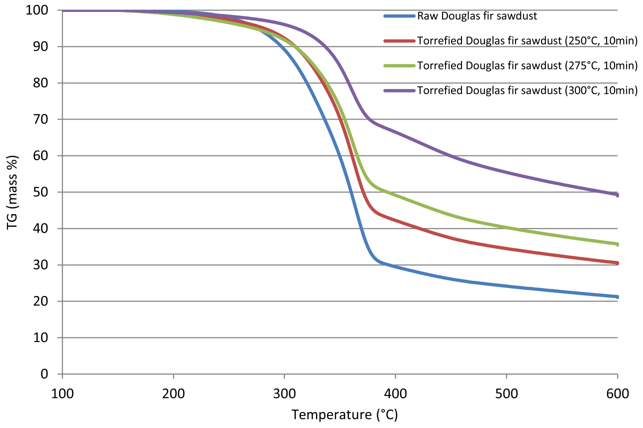

Fig. 4 – Thermogravimetric (TG) curves for raw and torrefied Douglas fir sawdust pyrolysis.

biomass with torrefaction temperature of 300 °C was due to the large mass loss along with the hemicelluloses and cellulose removal during torrefaction. The torrefied biomass formed more biochar in pyrolysis by cross-linkage reactions (Wannapeera et al., 2011).

The hemicelluloses and cellulose are decomposed fast at relatively low temperatures of 200–350 °C while lignin are decomposed slowly in a large range of temperatures from 280 to 600 °C. The maximum weight loss of hemicelluloses and cellulose occurred at the temperature 268 and 355 °C in a previous study for pure hemicelluloses and cellulose analysis (Yang, Yan, Chen, Lee, & Zheng, 2007). Generally, for biomass, the shoulder that is contributed by the decomposition of hemicelluloses can be observed at the temperature about 300 °C in DTG analysis (Muller-Hagedorn, Bockhorn, Krebs, & Muller, 2003; Yang et al., 2007). In our research, this shoulder was also observed for the raw Douglas fir sawdust pyrolysis (Fig. 5). However, for the torrefied biomass pyrolysis, the shoulder was eliminated, especially for the sample subjected to the high temperature torrefaction. The peak of DTG along with the maximum weight loss was mainly contributed by cellulose (Yang et al., 2007). In our study the peak of DTG curve for raw biomass pyrolysis was near 365 °C. The peaks of DTG curve for torrefied biomass pyrolysis were observed at the same temperature, indicating that the torrefaction had less effect on the temperatures of cellulose decomposition. However, the height of peak in torrefied biomass revealed the decreasing trend with the severity of torrefaction. The DTG peak of torrefied biomass with torrefaction temperature of 250 °C showed slight reduction compared to that of raw biomass, suggesting insignificant effects on cellulose in torrefaction. However, the DTG peaks of torrefied biomass were reduced significantly when the torrefaction temperature was increased to 300 °C due to the depletion of the majority of the biomass in the torrefaction. The increase in the peaks of the DTG curves for torrefied biomass was observed and the increase grew larger with the severity of torrefaction. This may be attributed to the decomposition of lignin and second reaction of biochar.

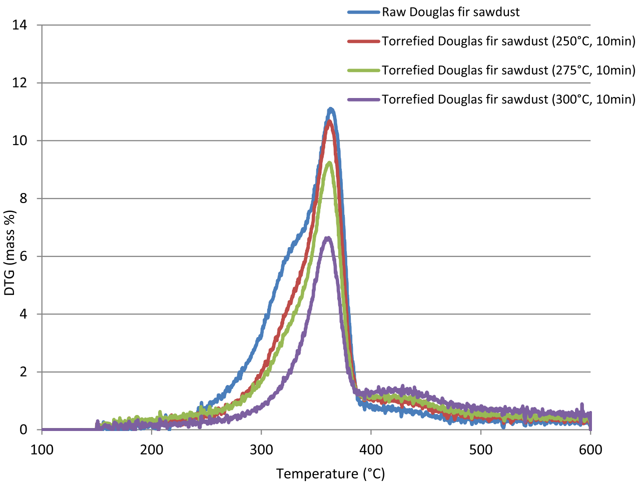

Fig. 5 – Derivative thermogravimetric (DTG) curves of raw and torrefied Douglas fir sawdust pyrolysis.

3.4. *One-step global kinetics of torrefied Douglas fir sawdust pyrolysis*

A one-step global kinetic model was used to describe the thermal decomposition of raw and torrefied Douglas fir sawdust pyrolysis, which can be schematised as:

$$\text{Raw/torrefied Douglas fir sawdust} \rightarrow \text{Bio-oiloil} + \text{Syngas} + \text{biochar} \tag{7}$$

The rate of decomposition of raw and torrefied Douglas fir sawdust pyrolysis can be expressed by Eq. (4). Eq. (4) was solved with the Friedman method to determine the values of kinetic parameters.

The Friedman method is an isoconversional method based on the assumption that the reaction rate ($d\alpha/dt$) at a constant conversion (α) is only a function of temperature (Friedman, 1964). The Eq. (4) can be rewritten as:

$$d\alpha/dt = A \cdot \exp(-E/RT) \cdot f(\alpha) \tag{8}$$

Converting Eq. (8) into a logarithmic expression we have:

$$\ln(d\alpha/dt) = (-E/RT) + \ln(Af(\alpha)) \tag{9}$$

Therefore, for the given value of conversion rate (α) the plot of $\ln(d\alpha/dt)$ versus $1/T$ gives a straight line with the slope of $-E/R$ and intercept of $\ln(Af(\alpha))$.

Figure 6 shows the plots of $\ln(d\alpha/dt)$ vs. $1/T$ for raw and torrefied Douglas fir sawdust. The fitted lines for raw Douglas fir sawdust were nearly parallel, indicating that the activation energies were rather close for different conversion rates and the mechanism of biomass pyrolysis was a one-step global reaction. The similar phenomenon was observed for the torrefied biomass at torrefaction of 250 °C and 10 min, implying that the torrefaction at the relatively low temperature did not change the reaction mechanism of pyrolysis. Figure 6c shows the plots for torrefied biomass at the torrefaction temperature of 275 °C. The fitted lines in the conversion rate of 0.1–0.7 were nearly parallel. For the very low (<0.1) or high (≥ 0.8) conversion rates, the fitted lines are slightly diverged from the parallel lines, implying a change in the trend with the increase in torrefaction temperature due to the different reaction mechanism for torrefied biomass. The plots for the torrefied biomass with the torrefaction temperature of 300 °C illustrated that the fitted, nearly parallel lines can only be observed at the conversion rate of 0.2–0.5 (Fig. 6d). This confirmed that the torrefaction processes at relatively high temperatures substantially influenced the reaction mechanism. The multiple-step reactions, instead of one-step global reactions, might occur in such torrefied biomass. These observations were consistent with the findings on DTG curves analysis.

The average activation energies were summarised in Table 3. The average activation energy for the raw biomass was 204 kJ mol^{-1}, slightly higher than those reported in previous studies for woody biomass pyrolysis (Blasi, 2008; Blasi & Branca, 2001; Gronli, Varhegyi, & Blasi, 2002). The average activation energies of torrefied biomass ranged from 198 to 195 kJ mol^{-1}, which were slightly lower than for the raw biomass. However, the difference in the activation energies between raw biomass and torrefied biomass showed no significance (T-test, $P > 0.05$). The reduction was increased with

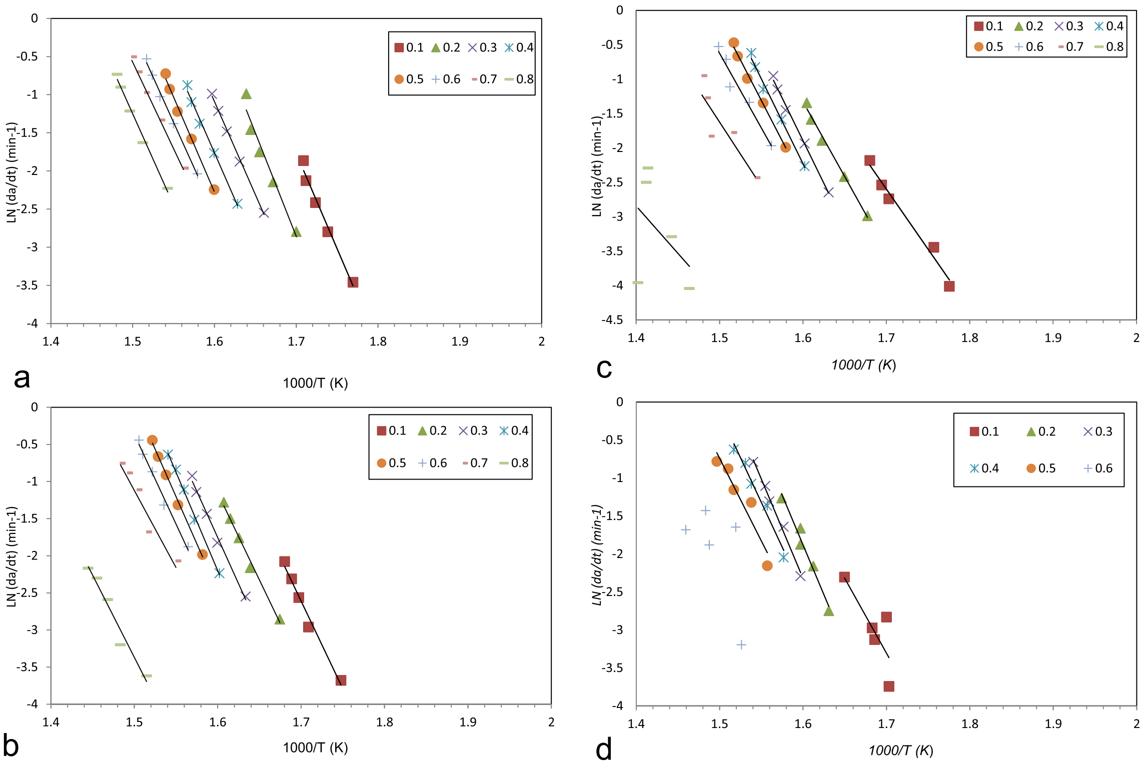

Fig. 6 – Isoconversional plot for (a) raw and torrefied Douglas fir sawdust, (b) torrefaction of 250 °C and 10 min, (c) torrefaction of 275 °C and 10 min, and (d) torrefaction of 300 °C and 10 min.

the severity of torrefaction. This may be attributed to the concentration of mass and modified structure in the cellulose and lignin in torrefied biomass. These changes in the biomass may have eased the decomposition process during pyrolysis. The high R-square value of the fitted model suggests that the one-step, first-order reaction model can adequately describe the raw and torrefied Douglas fir sawdust pyrolysis.

4. Conclusion

The thermal decomposition behaviours and kinetics of Douglas fir sawdust torrefaction and raw and torrefied Douglas fir sawdust pyrolysis were investigated using thermogravimetric analysis. The sample mass loss in torrefaction was highly related to the torrefaction temperature. The two-step model fits well for Douglas fir sawdust torrefaction. The activation energies of the first and second reaction stages were 112 kJ mol^{-1} and 150 kJ mol^{-1}, respectively.

Raw and torrefied Douglas fir sawdust illustrated different thermal decomposition behaviours. The decomposition of torrefied biomass shifted to high temperature and the degree of the shift increased with the severity of torrefaction. DTG analysis revealed that the decomposition of hemicelluloses in torrefied biomass was reduced or even eliminated at the high torrefaction temperature. However, the decomposition rate of torrefied biomass has a decreasing trend due to the mass depletion in torrefaction. The first-order, one-step global model with the average activation energies in the range of 203.94–195.13 kJ mol^{-1} can describe the raw and torrefied biomass pyrolysis. The slightly decreasing trend of activation energy was observed for the torrefied biomass pyrolysis compared to the raw biomass. The kinetic analysis showed that the torrefied biomass subject to high torrefaction temperatures may involve multiple-step reactions.

Table 3 – Average apparent activation energy, log A and R^2 of the models for raw and torrefied Douglas fir sawdust calculated by the Friedman method for first-order reactions.

Biomass	Activation energy (kJ mol^{-1})	log A (min^{-1})	R^2
Raw Douglas fir sawdust	204 (10. 8)	16.6 (1.22)	0.988 (0.012)
Torrefied Douglas fir sawdust (250, 10 min)	198 (15.2)	15.8 (1.49)	0.980 (0.022)
Torrefied Douglas fir sawdust (275, 10 min)	197 (33.9)	15.5 (2.17)	0.9911 (0.009)
Torrefied Douglas fir sawdust (300, 10 min)[a]	195 (23.7)	15.5 (1.93)	0.8976 (0.143)

[a] $\alpha = 0.1–0.5$.

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